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Molecular collision studies at Princeton are reviewed. The areas of research involved are:

(1) CO laser kinetics;
(2) Global Collision Theory;
(3) Quantum Number Scaling and the Analysis of Spectral Line Shapes;
(4) Stochastic Theory of Molecular Collisions; and
(5) Vibration-Rotation Relaxation in Molecular Collisions.

Technical Report

Report No. Pr-5

COLLISION STUDIES OF GASEOUS MOLECULAR LASERS

by

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REPORT SUMMARY

Research is under way into various aspects of molecular collision theory. A prime goal of this work is the analysis of collisional relaxation phenomena relevant to laser operation. The CO system is being extensively studied as an example in collaboration with Professor E. Fisher, Wayne State University. In more general terms a variety of techniques are being developed and applied to study collisions under many different experimental situations. Progress on this research is summarized below.

(1) Kinetics of the CO Laser and Related Relaxation Phenomena

In collaboration with Ed Fisher, Wayne State University, we have analyzed the population distribution produced in a CO-He electric discharge at 150^0 K. Our new scaling theory for CO rates was incorporated in the analysis, and the experiments confirm the rate behavior. It is observed that the vibration-vibration pumped plateau is very broad and extends to high quantum numbers ($v > 30$). The analysis shows how the underlying vibration-vibration and vibration-translation rates interplay to produce this plateau. This work has important implications for laser performance in relation to the implied ease of dissociation which can affect the plasma, optics, power, etc.

1. E. Fisher, H. Lam, and H. Rabitz, Kinetic Analysis of CO-He Electric Discharges, manuscript in preparation.

(2) Global Scattering Theory for Reactive and Non-Reactive Collisions

A new collision method is being developed which promises large savings by the use of global wavefunctions. The normal close-coupling approach expands all variables except one in a chosen basis and thereby leads to coupled ordinary differential equations. The global approach expands all variables except two and leads to fewer coupled partial differential equations. With the availability of efficient partial differential equation codes, the global approach has an important advantage in cases where the extra coordinate would require many basis functions by conventional close coupling. Within the global theory we have shown how to obtain state-to-state as well as total cross sections. The global approach has the attractive feature of allowing for the computation of total cross sections directly without recourse to individual state-to-state cross sections. This aspect is particularly significant for complex systems. The possible use of finite element methods for treating the partial differential equations is being explored. The most important immediate applications of this method are to chemical reactions and electron impact excitation. These activities are being pursued.

1. H. Rabitz, A. Askar, and A. Cakmak, The Use of Global Wavefunctions in Scattering Theory, J. Chem. Phys., submitted.

2. A. Askar, A. Cakmak, and H. Rabitz, Finite Element Method for Reactive Scattering Calculations in Quantum Mechanics, J. Chem. Phys., submitted.

(3) Quantum Number and Energy Scaling of Collisions with Application to Spectral Line Shape Analysis

A general formula for rotationally inelastic cross sections in atom-diatomic collisions has been derived. This result was achieved by assuming the transition probability is a function of rotational quantum number differences, the kinetic energy in the upper states, and is inversely proportional to the number of accessible states within an effective Hamiltonian formalism. The scaling law is able to predict all rows or columns of the inelastic cross section matrix, $\sigma_{jj'}$, given any one row or column as a function of energy. We have applied this scaling theory to a variety of collision systems; in general, good agreement between predicted and exact results is exhibited. The theory has been taken a step further to predict scaling behavior of rate constants, $k_{j\to j'}$. This information has allowed us to extract rate constants from line shapes provided they extend over several j transitions. This development significantly increases the usefulness of line shape measurements as a source of rate data.

1. A. DePristo and H. Rabitz, Quantum Number and Energy Scaling of Rotationally Inelastic Scattering Cross Sections, Chem. Phys., in press.

2. A. DePristo and H. Rabitz, Extraction of Rate Constants from Spectral Line Shape Measurements, manuscript in preparation.

(4) Stochastic Theory of Molecular Collisions

This research represents an effort to develop a theory capable of handling strong molecular collisions. Such strong collision problems cannot be treated by conventional techniques. We have reported previously on the initial developments of the theory and significant progress has recently been made.

Previous research considered describing molecular collisions by the techniques of non-equilibrium statistical mechanics. This stochastic theory of molecular collisions has been applied to vibration-rotation inelasticity in a He-H_2 system. Some changes in the theory were made in order to better handle energetic effects particularly important in the weak coupling limit. The resulting formulation leads to the solution of simultaneous Fokker-Planck and master equations for the rotational and vibrational motion, respectively. The cross sections were computed for total energies from 1.3 eV to 4.0 eV. At this highest energy 85 vibration-rotation states were energetically accessible. Very strong near-resonant vibration-rotation inelasticity was found from the high rotational levels ($j \sim 18$).

Although the original theory was designed to handle strong collisions, we have also carefully examined the perturbation (weak-coupling) limit of the theory. It was shown how the formulation reduces to exact quantum mechanics in the perturbation regime. The results of this work and previous research show that stochastic collision theory firmly connects up to both the weak and strong coupling limits. It is suggestive that computationally attractive schemes which afford reasonable accuracy can now be developed for the

intermediate coupling regime as well. We firmly believe the stochastic theory will form the basis of a new generation of practical collisional techniques. Research toward this goal will continue.

1. S. Augustin and H. Rabitz, Application of Stochastic Theory to Vibration-Rotation Inelasticity, J. Chem. Phys., in press.

2. S. Augustin and H. Rabitz, Stochastic Theory for Molecular Collisions in the Perturbation Limit, J. Chem. Phys., submitted.

(5) Vibration-Rotation Relaxation in Molecular Collisions

An efficient and accurate second-generation computer code has been developed to rapidly scan a variety of collision processes. The program can handle cases up to symmetric top molecules. Probing studies are under way to discern key molecular parameters controlling collision behavior. In a related piece of work a detailed vibration-rotation-translation quantum calculation on H_2-H_2 was performed. This case is of interest in its own right as well as forming a useful model for more complex systems. The detailed mechanism of relaxation was examined in these calculations. Studies such as these will continue and they are capable of providing valuable information for laser design and related applications.

1. S. Tarr and H. Rabitz, An Efficient and Accurate Program for the Analysis of Molecular Collisions, manuscript in preparation.

2. R. Ramaswamy and H. Rabitz, Vibration-Rotation Relaxation in Bimolecular Collision with Application to Para-Hydrogen, J. Chem. Phys. 66, 152 (1977).